Design and Characterization of Photo-responsive Supramolecular Aggregates

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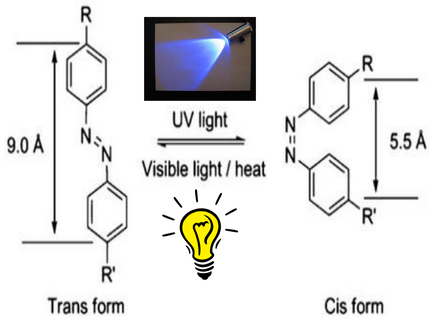
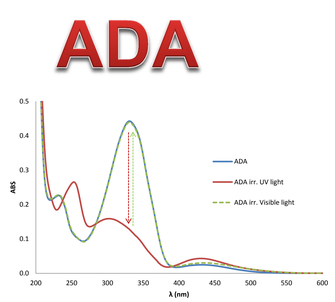
Introduction

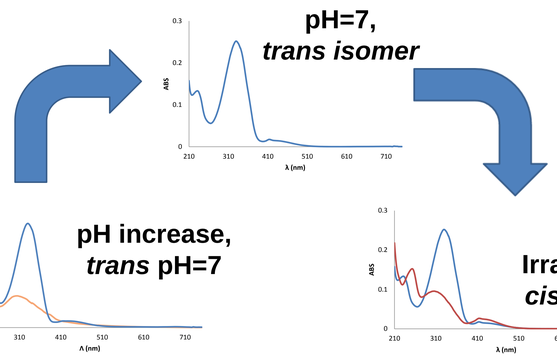
Supramolecular chemistry concerns the manner in which molecular building blocks associate via non-covalent interactions and form aggregates. The particular building block in this research is ADA, a molecule that isomerizes reversibly around an N-N double bond upon irradiation with different wavelengths of light. The large structural changes in the molecule that result from isomerization have the potential to modulate the properties of a supramolecular aggregate.

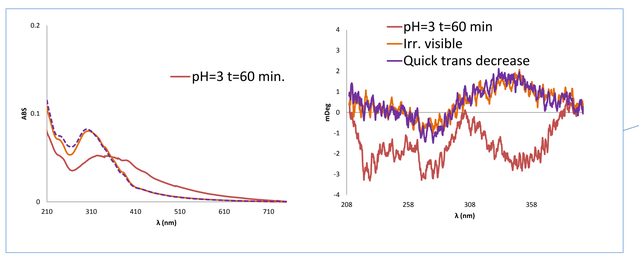
Abstract

The photo-responsive molecule 4,4'-azobenzene dicarboxylic acid (ADA) was studied under a variety of environmental conditions for the purpose of understanding aggregation behavior and geometries. The data show that self-aggregation of ADA at low pH is under hierarchical control giving rise to the formation of a variety of structures dependent on the procedure for their formation; typically, the aggregates have a preferential asymmetric geometry despite the symmetry of the constituent molecules. Moreover, the use of a chiral template macromolecule (poly-glutamate) during the formation of the aggregate can affect the structure of the supramolecular species and direct its chirality. Finally, the aggregates containing the *cis* isomer of ADA were shown to retain their ability to photo-isomerize to the aggregates of the *trans* form.







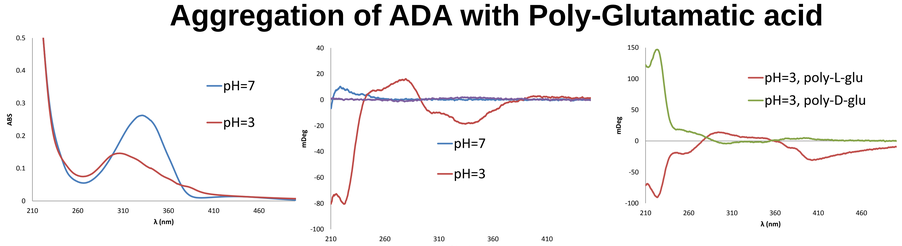


Fast pH decrease of *cis*-ADA forms an aggregate, but switches back to the *trans* isomer upon irradiation with visible light forming an aggregate super-imposable with the one obtained by reducing quickly the pH of a solution of *trans*-ADA

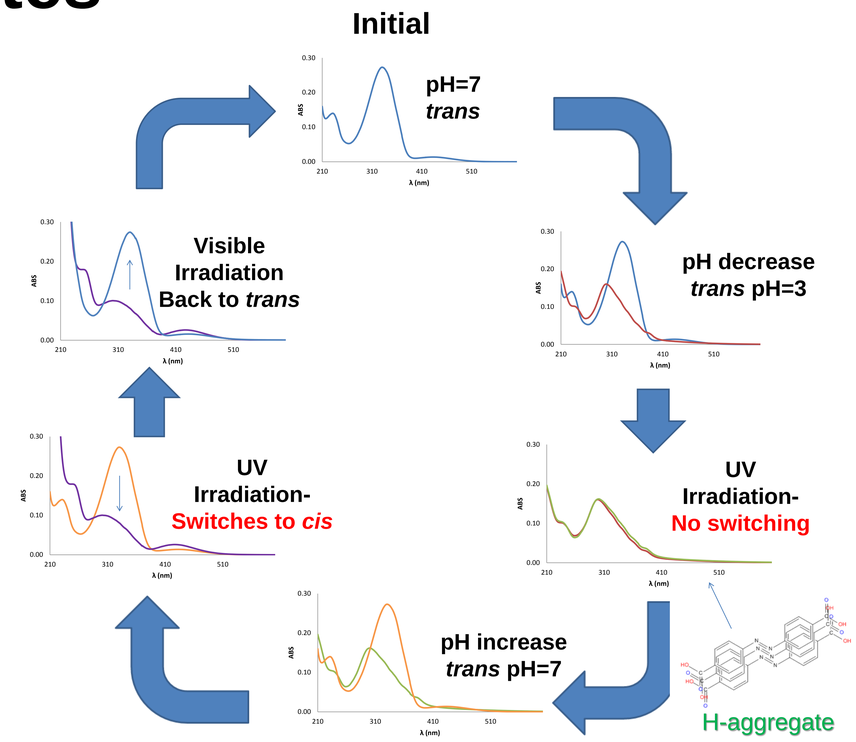
Materials and Methods

- Absorption (UV-Vis) and Circular Dichroism (CD) measurements were performed with a Jasco V-630 and J-815, respectively. UV irradiation was performed using a 100 Watt Hg Lamp (365 nm).
- Both UV and visible irradiation were performed at basic or acidic pH for 15 min intervals.
- The aggregates explored were *cis*- or *trans*-ADA alone and in the presence of poly-Glutamic acid; low pH conditions were obtained by decreasing the pH from 7 to 3 in one step (fast) or in steps of 0.5 pH units (slow).

Aggregation of ADA with Poly-Glutamatic acid



The presence of poly-L-Glu promotes the formation of a chiral aggregate of ADA with a very intense CD signal. The inversion of the signal related to the aggregate when poly-D-Glu is used shows that the chirality is induced by the template.



Fast pH decrease of *trans*-ADA results in formation of an H-aggregate, that will prevent the isomerization to the *cis* form upon irradiation with UV light. Molecule regains photoswitching capabilities upon pH increase and disaggregation.

Conclusions

When the pH of a *trans*-ADA solution is quickly reduced from 7 to 3, a blue shift and hypochromicity of the absorption band indicate that a parallel assembly, known as an H-aggregate, is formed. In this geometry, both π−π stacking and hydrogen bonds are possible, making the aggregate very compact and strong and preventing *trans*-ADA from photoswitching. If the pH is brought back to 7, the *trans*-ADA returns to its monomeric form and is able to photoisomerize again.

When the pH of a solution of mainly *cis*-ADA is quickly reduced from 7 to 3, a red shift and hypochromicity of the absorption band indicate that an assembly with a head-to-tail orientation, known as a J-aggregate, is formed. The less packed geometry allows for photoisomerization. After irradiation with visible light, the *cis*-ADA switches back to the *trans*-ADA and gives rise to the formation of an aggregate that is analogous to the aggregate obtained upon quickly decreasing the pH of the *trans*-ADA monomer as the superimposition of the UV-Vis band and the CD spectra show. Finally, the introduction of a chiral template, poly-L-Glutamic acid, during the aggregation process was shown to direct the formation of a new asymmetric aggregate that has a chirality induced by the polymer as shown by the inversion of the signal of the ADA aggregate when it forms in the presence of the poly-D-Glu.